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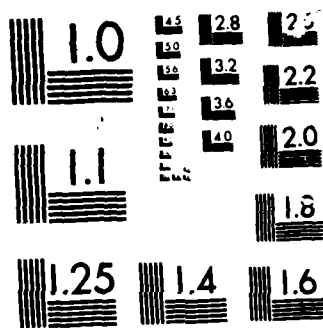
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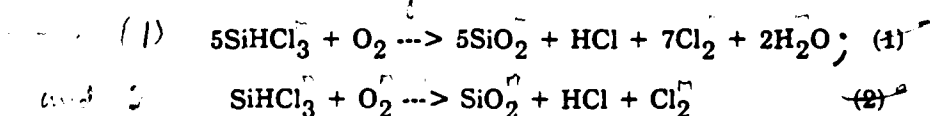
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ABSTRACT

Various properties and reactions of trichlorosilane (SiHCl_3) have been studied to obtain information on the combustion of trichlorosilane. The infrared absorption spectra, impact flammability results and the heat of formation of SiHCl_3 are included in this paper. The production of silicon from trichlorosilane by thermal decomposition and hydrogen reduction is reviewed to point out certain reaction characteristics of SiHCl_3 .

The combustion of trichlorosilane is studied in detail. Two reactions are proposed as being the combustion reaction and are as follows.



Having no basis on which to determine which of the two reactions is the actual combustion reaction, both are considered in this paper. The theoretical heat of combustion for reaction 1 is -815.3 cal/g and for reaction 2 is -774.9 cal/g. Combustion experiments were performed with trichlorosilane using a Parr semimicro calorimeter. The amount of SiHCl_3 lost by evaporation between the time the sample was weighed and ignited was estimated. Using this corrected mass value, the heat of combustion of trichlorosilane was found to be -803.8 cal/g, which tends to indicate that reaction 1 above, dominates.

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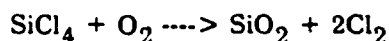
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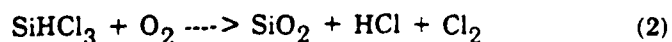
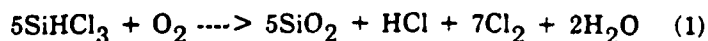
Chapter I

INTRODUCTION

Interest in the combustion properties of trichlorosilane arose during research aimed at improving the existing methods of preparing glass preforms that can be drawn into optical fibers. Currently, the reaction of silicon tetrachloride with oxygen is used in particle deposition processes to obtain optical fiber grade silicon dioxide.



Although the combustion of silicon tetrachloride is an exothermic reaction, the reaction does not proceed until the temperature of the reactants reaches 1200°C. As a possible alternative to this reaction for producing silicon dioxide, we wish to consider the substitution of silicon tetrachloride by trichlorosilane. This provides the motivation for our literature survey into the various physical properties of trichlorosilane and for our examination of the heat of reaction of trichlorosilane with oxygen. The combustion of trichlorosilane is an exothermic reaction and readily occurs at low temperatures when initiated by a spark or heat lamp. Based on information in the literature [2, 14], the combustion of trichlorosilane proceeds according to one of the following reactions.



Chapter II

LITERATURE SURVEY

Unfortunately, there is little information in the literature on the oxidation of trichlorosilane, SiHCl_3 . Various reactions are proposed for the combustion reaction of trichlorosilane, and they are discussed in this section. The production of pure silicon is the most common application in which trichlorosilane is used. Various techniques utilizing thermal decomposition and hydrogen reduction of SiHCl_3 are employed to obtain pure silicon. Some of these processes are described later in this section in an effort to point out certain reaction characteristics of trichlorosilane. Additional information is available on the general properties, absorption spectras, impact flammibility, and heat of formation of trichlorosilane and is incorporated into this section.

2.1 GENERAL PROPERTIES

Trichlorosilane is a clear, flammable liquid with a suffocating odor. It is also highly volatile and corrosive which makes it very difficult to handle. Table 1 lists the properties of trichlorosilane as given in the Alfa Catalogue [1].

TABLE 1
Properties of SiHCl_3

Molecular Weight	135.45
Liquid	
Melting Point	-126.5° C
Boiling Point	33° C at 758mm
Density	1.34 g/cm ³
Refractive Index	1.402C

2.2 ABSORPTION SPECTRA

The characteristic infrared absorption bands for trichlorosilane lie in the 2100 to 2300 cm^{-1} range and in the region below 900 cm^{-1} . The SiHCl_3 infrared absorption spectra is given in Figure 1 [3,p.36].

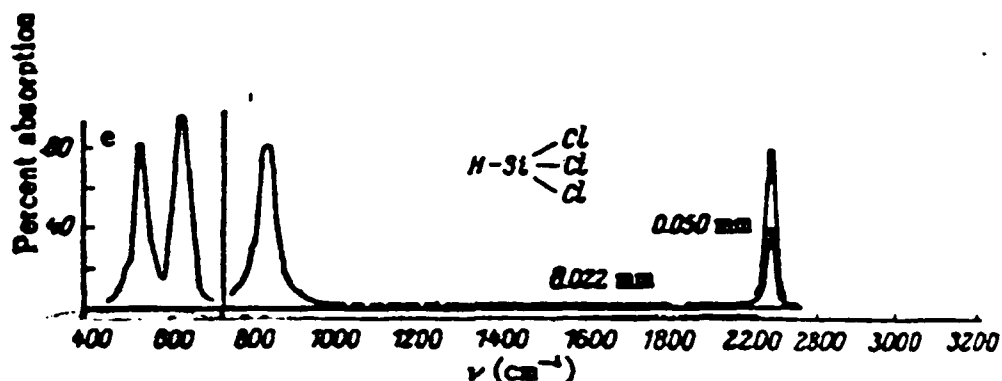


Figure 1: IR absorption spectra of SiHCl_3 .

Chumaevskii [3] indicates that the vibration of the Si-H bond is responsible for the sharp absorption band at 2262 cm^{-1} and the band at 802 cm^{-1} is due to the bending of the Si-H bond. In addition, Chumaevskii associates the Cl_3 functional group with the absorption bands in the 450-490 cm^{-1} and 570-600 cm^{-1} ranges.

The infrared spectra of trichlorosilane in the liquid and vapor states, in terms of percent transmission, are shown in Figure 2 [4,p.1432] and Figure 3 [4,p.1432] on the following page. Gibian and McKinney [4] go into great detail by assigning combinations of characteristic modes to each absorbed frequency. Two fundamental frequencies for trichlorosilane in the liquid and vapor states are observed at approximately 800 cm^{-1} and 2260 cm^{-1} . Gibian and McKinney assign the 808 cm^{-1} (vapor) and the 798 cm^{-1} (liquid)

bands to the Si-H bending mode. The 2274 cm^{-1} (vapor) and the 2258 cm^{-1} (liquid) bands are attributed to the vibration of the Si-H bond. It should be noted that Gibian and McKinney's work was the only found in which the infrared absorption spectra of liquid trichlorosilane was given.

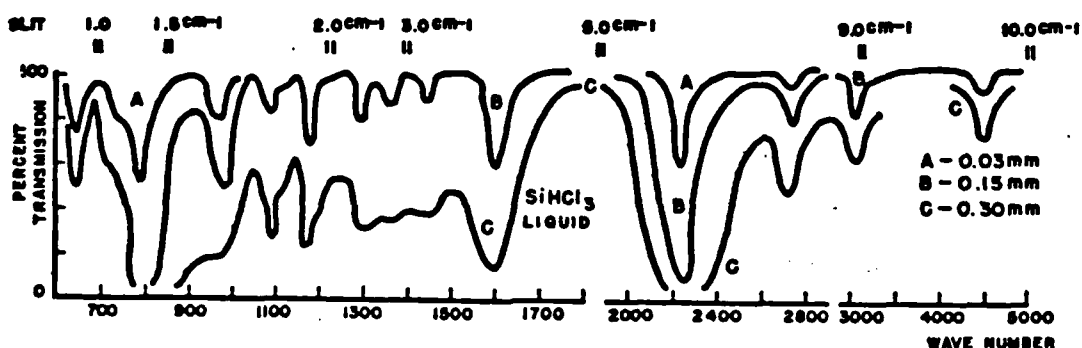


Figure 2: IR spectrum of SiHCl_3 liquid.

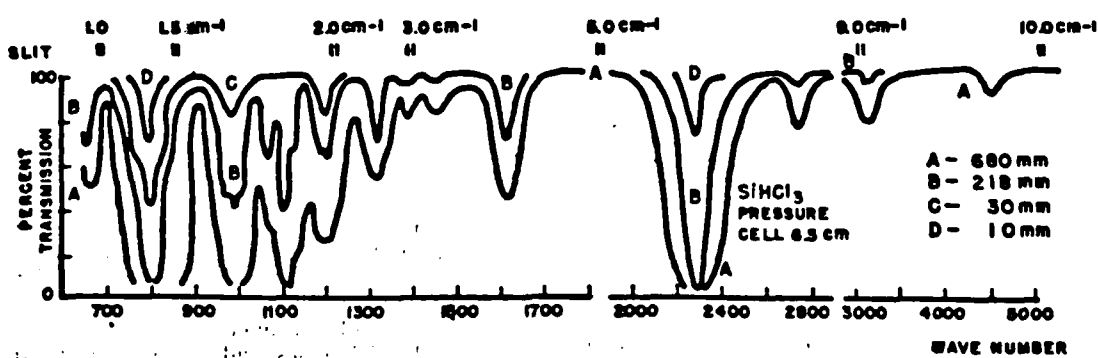


Figure 3: IR spectrum of SiHCl_3 vapor.

Shimanouchi's Table of Molecular Vibrational Frequencies [5] for gaseous trichlorosilane provides a list of each mode and its associated infrared absorption frequency. In addition, the Raman spectra of liquid trichlorosilane is included in this table. The letter code after the selected frequency value is an indication of the accuracy of the value. The letters run from A to E. The letter code after the infrared frequency gives an estimate of the intensity of the band. VS indicates very strong, S indicates strong while M indicates medium. And finally, the code after the Raman frequency indicates whether the shift is due to a polarized or depolarized electron state. A copy of this table is included as Table 2 [5,p.1028].

TABLE 2
Molecular vibration frequencies of SiHCl_3

No.	Approximate type of mode	Selected value of frequency	Infrared	Raman
		cm^{-1}	cm^{-1} (Gas)	cm^{-1} (Liquid)
ν_1	SiH stretch.	2261 B	2260.9 S	2258 p
ν_2	SiCl_3 s-stretch.	499 B	498.6 S	489 p
ν_3	SiCl_3 s-deform.	254 B	253.7 M	250 p
ν_4	SiH bend.	811 B	810.8 VS	799 dp
ν_5	SiCl_3 d-stretch.	600 B	600.1 VS	587 dp
ν_6	SiCl_3 d-deform.	176 B	175.5 M	179 dp

Little information is available concerning the absorption of SiHCl_3 in the ultraviolet or visible range. Nagata, Dohmara, Fujita, Oka and Taniguchi [6] studied particle formation

from gas phase silicon compounds including SiHCl_3 by light or electron irradiation. Photo-irradiation was performed using a 500W xenon lamp or a 500W high pressure mercury lamp. Electron irradiation was done with 10MeV electrons from a linear accelerator. It was found that trichlorosilane did not absorb light from the xenon or mercury lamp. Particle formation from trichlorosilane was observed only after electron beam irradiation. Clearly, more work must be done to completely determine and understand the absorption characteristics of SiHCl_3 in the ultraviolet and visible spectras.

2.3 SILICON PRODUCTION

According to the literature, the most common application of trichlorosilane is the production of high purity silicon. Silicon deposition from the thermal decomposition of trichlorosilane occurs at temperatures above 480°C [7]. The yield of silicon, expressed as a percent, is defined as the ratio of the weight of silicon gained to the total weight of silicon atoms in the trichlorosilane used, multiplied by a factor of 100. Blocher, Browning and Wilson [8] show that the yield of silicon from the thermal decomposition of trichlorosilane is temperature sensitive. Figure 4 [8,p.152] on the following page shows that at atmospheric pressure the greatest yields of Si occur from 900°C to 1100°C . Within this temperature range, Yoshizawa, Hashino and Sakaguchi [7] studied the rate of deposition and the yield of silicon in relation to the feeding rate of trichlorosilane. Figure 5 [7,p.6] shows the relationship of the feed rate of trichlorosilane to the deposition rate of silicon at 950°C , 1000°C and 1100°C . Figure 6 [7,p.7] gives the relationship between the yield of silicon and the feed rate of trichlorosilane. From all three figures, the conclusion can be made that both the silicon deposition rate and the silicon yield are maximum at 1000°C .

A method commonly used to increase the yield of silicon from trichlorosilane is hydrogen reduction. While hydrogen reduction increases the yield of silicon per gram of SiHCl_3 , the addition of hydrogen reduces the concentration of SiHCl_3 . Therefore, to maintain a high deposition rate while increasing the yield, the feed rate of trichlorosilane

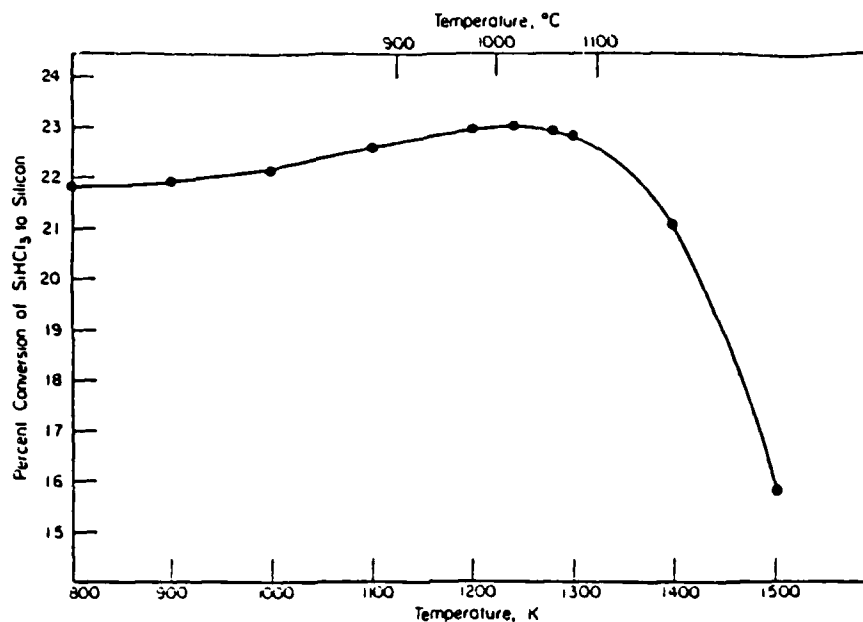


Figure 4: Temperature vs. Equilibrium Decomposition of SiHCl_3

must increase. However, if the feed rate of trichlorosilane is increased too much, the yield of silicon begins to decrease. A detailed description of the hydrogen reduction process and the effects of hydrogen reduction and other parameters on silicon production are given later in this section.

Based on the observation that silicon is produced during the thermal decomposition of trichlorosilane, Yoshizawa, Hashino and Sakaguchi [7] looked into the possibility that silicon deposition from the thermal decomposition of SiHCl_3 without any added reductants could be a feasible way of producing silicon. They proceeded by examining the reaction products in an effort to understand the equilibrium composition and the reaction methods involved. For reaction temperatures greater than 700°C , a glass reactor was used equipped with tungsten wire or tantalum foil connected to electrodes on the reactor top for heating the reaction gas. The walls of the glass reactor were cooled and maintained at

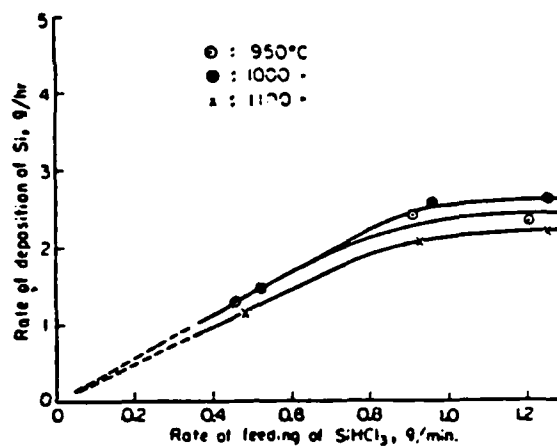


Figure 5: SiHCl_3 feed rate vs. Si deposition rate.

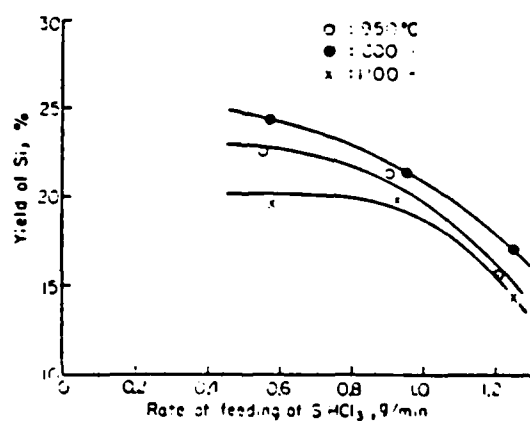
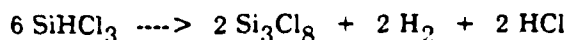
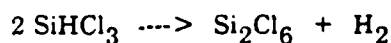


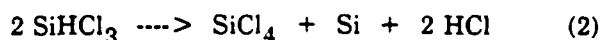
Figure 6: SiHCl_3 feed rate vs. Si yield.

60° C. For reaction temperatures less than 700° C, a quartz reactor was used and an electrical furnace outside the reactor was used to heat the trichlorosilane. The silicon deposited on various surfaces during the reaction, on the tungsten wire or tantalum foil in the glass reactor and on the inside wall of the quartz reactor.

H₂, SiH₄, and unreacted SiHCl₃ appear in significant amounts in the gaseous product of this decomposition. When the decomposition occurs at temperatures greater than 850° C, gaseous HCl is also produced in significant amounts. In addition, Yoshizawa, Hashino and Sakaguchi [7] reported finding a transparent, oily liquid inside the glass reactor which turned into a white solid when coming into contact with air. This liquid product is assumed to be a mixture of higher molecular weight compounds of silicon and chlorine which thermally decompose into Si and SiCl₄. The polymerizing reactions they believe produce this transparent, oily liquid are as follows.



By analysing the composition of the equilibrium mixture in the reactor, Yoshizawa, Hashino and Sakaguchi [7] propose that the thermal decomposition proceeds according to the following simultaneous reactions.



Assuming that these are the three significant reactions, the equilibrium constant for each is found and the extent of each reaction as a function of temperature is determined [7]. Figure 7 [7,p.17] shows that although the extent of each individual reaction varies with

temperature, the thermal decomposition of trichlorosilane which is the sum of the three reactions listed above goes almost to completion over the temperature range from 600° C to 1400° C. Since silicon is not produced in the third reaction, there is clearly a point of maximum silicon yield within the 600° C to 1400° C temperature range. As previously shown, the point of maximum silicon yield occurs at approximately 1000° C. Figure 8 [7,p.17] on the following page indicates that the yield of silicon starts to decrease at temperatures greater than 1000° C. Yoshizawa, Hashino and Sakaguchi [7] attribute this to the formation of silicon dichloride and other higher molecular silicon and chlorine compounds at high temperatures.

The conversion ratio of trichlorosilane to high purity silicon by thermal decomposition is found to be very low. Blocher, Browning and Wilson [8] find that the maximum silicon yield is approximately 23 percent, occurring in the 900° C to 1000° C temperature range. (Refer to Figure 4) Based on similar findings, Yoshizawa, Hashino and Sakaguchi [7] conclude that the thermal decomposition of trichlorosilane alone is not an efficient way of producing silicon. They attribute this low conversion rate to the number of reactions involved and their complexities. Therefore, hydrogen reduction of trichlorosilane must be used to produce pure silicon in high yield.

The hydrogen reduction of trichlorosilane takes place according to the following reaction.



Yoshizawa, Hashino and Sakaguchi [7] define the reacting ratio of trichlorosilane as the ratio of reacted SiHCl_3 to the amount of SiHCl_3 initially present. It is found that the reacting ratio of SiHCl_3 increases as r , the mole ratio of H_2 to SiHCl_3 increases [7]. At low values of r , the dominant reactions are the thermal decomposition reactions. At values of r equal to or greater than 10, hydrogen reduction becomes the dominant reaction. Therefore, high purity silicon can be produced in high yield by increasing the mole ratio of

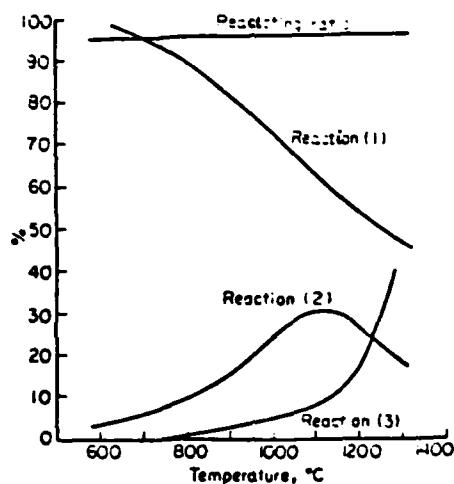


Figure 7: Temperature vs. reacting ratio of 3 SiHCl_3 reactions.

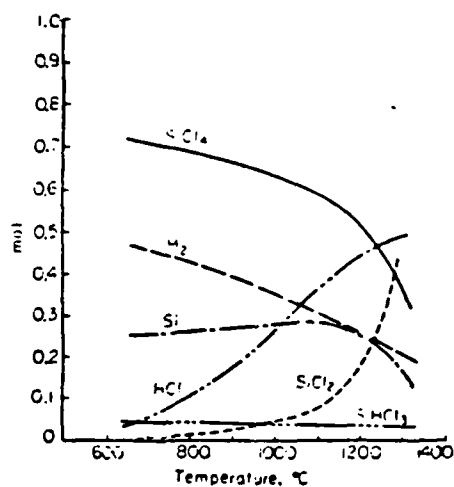


Figure 8: Temp. vs. moles of SiHCl_3 decomp. reaction products.

hydrogen to trichlorosilane. Figure 9 [7,p.24], shows the relationship between the mole ratio and the dominating reaction at 1500° K.

Reaction temperature is still an important parameter when looking at the reacting ratio of SiHCl_3 vs. the ratio of H_2 to SiHCl_3 . Figure 10 [7,p.24] indicates that for fixed

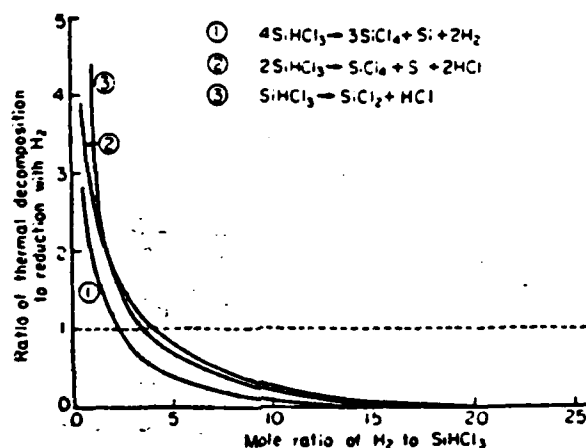


Figure 9: Mol ratio of H_2 to $SiHCl_3$ vs. $SiHCl_3$ reacts.

values of r , the reacting ratio of trichlorosilane increases with temperature. Figure 9 and Figure 10 show that at $1500^\circ K$ a $SiHCl_3$ reacting ratio of close to 100 percent can be achieved for a minimum mole ratio of H_2 to $SiHCl_3$ of 15. It appears that for a high enough ratio of H_2 to $SiHCl_3$ and at a high enough temperature, a 100 percent yield of silicon is theoretically possible. Clearly, there must be a tradeoff in this case. The silicon deposition rate decreases as the hydrogen to trichlorosilane ratio increases. As previously shown, it is possible to increase the deposition rate by increasing the $SiHCl_3$ feed rate. The balance between the feed rate, deposition rate, hydrogen to trichlorosilane ratio and reaction temperature must be made based on economic considerations.

Silicon deposition from trichlorosilane is usually a combination of thermal decomposition and hydrogen reduction. Nishizawa and Saito [9] used infrared absorption spectroscopy to study the reaction mechanisms of silicon chemical vapor deposition from thermal decomposition and hydrogen reduction with $SiHCl_3$ as the source material. The experiment involved feeding a mixture of $SiHCl_3$ and H_2 through a hot walled horizontal

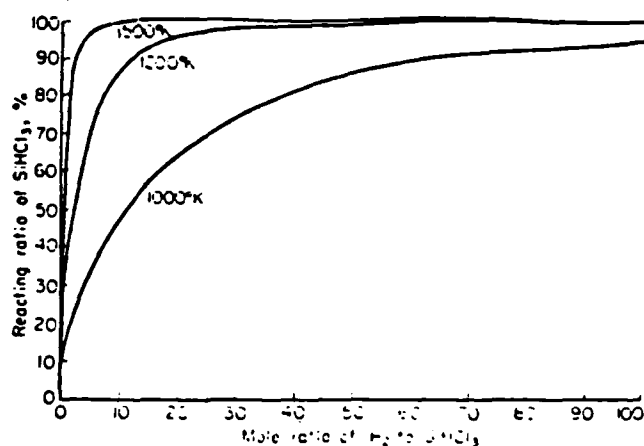
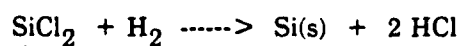
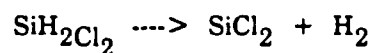
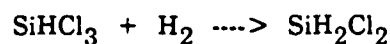
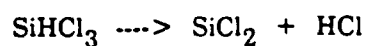


Figure 10: H₂ to SiHCl₃ mol ratio vs. SiHCl₃ react. ratio.

reactor. Both direct IR spectroscopy and IR spectroscopy by the sample method were used to determine the silicon-hydrogen-chlorine reactants present during the process. The following reactants were observed: SiCl₄, SiHCl₃, SiH₂Cl₂, HCl, SiCl₃, and SiCl₂.

Nishizawa and Saito [9] conclude that silicon chemical vapor deposition from trichlorosilane in an hydrogen atmosphere at temperatures in the 800° C to 1200° C range proceeds according to the following reactions.



By comparison with their results for the same process except with silicon tetrachloride substituted for trichlorosilane, the reaction mechanism shown in Figure 11 [9,p.218] is proposed.

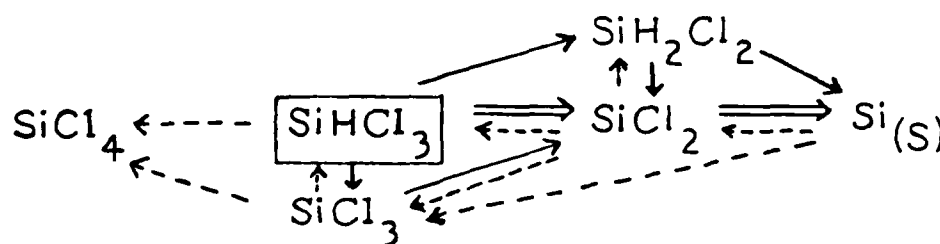


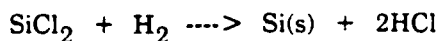
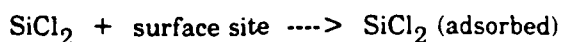
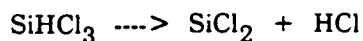
Figure 11: The SiHCl_3 and H_2 reaction mechanism.

Another important area of research concerning silicon production from trichlorosilane is the kinetics of the thermal decomposition and hydrogen reduction involved. Bloem, Claasen and Valkenburg [10] studied the reaction kinetics of silicon growth from trichlorosilane at temperatures less than 1000°C . At temperatures greater than 1000°C , the expected rate of silicon growth based on equilibrium calculations closely approximates the observed growth rate. Jones and Shaw [11] show that at these temperatures the kinetics of silicon growth can be attributed to the gas phase diffusion of reactants towards the growing silicon surface.

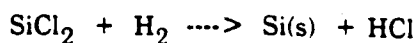
Bloem, Claasen and Valkenburg [10] point out that at temperatures less than 1000°C , silicon growth rates no longer follow those predicted from equilibrium

calculations. They propose that at lower temperatures, the rate of surface reactions decrease and the surface reactions become the rate limiting step. By analogy with their previous study on the kinetics of silicon growth from SiH_2Cl_2 [12], Bloem, Claasen and Valkenburg assume that SiCl_4 is the main surface species in the growth of SiHCl_3 as it was in the case of SiH_2Cl_2 . Since SiCl_2 reduces to silicon in the presence of hydrogen, it is expected that the growth rate of silicon from SiHCl_3 at temperatures less than 1000°C is a function of hydrogen partial pressure.

Bloem, Claasen and Valkenburg [10] tested their proposal experimentally by studying silicon growth from SiHCl_3 using $\text{SiHCl}_3\text{-H}_2\text{-N}_2$ as the reacting mixture in a horizontal reactor operating at atmospheric pressure. Studies were done at 800°C , 900°C and 1000°C , and at various hydrogen partial pressures. Silicon growth occurred on top of a thin silicon layer on a substrate that was placed in the reactor. Again, the results showed that the silicon growth rate increases with increasing hydrogen pressure and was greatest at 1000°C . The proposed reaction steps for silicon deposition in the presence of hydrogen at temperatures less than 1000°C are as follows [10].



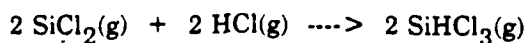
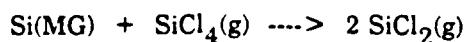
The SiHCl_3 undergoes a gas phase reaction which produces SiCl_2 and HCl . This is followed by the SiCl_2 adsorption on the silicon surface and the reduction of SiCl_2 by hydrogen to Si and HCl . As expected from these reaction steps, the addition of HCl to the gas phase decreases the silicon growth rate. Based on their findings, Bloem, Claasen and Valkenburg [10] propose the following step as the rate limiting step in the silicon vapor deposition from trichlorosilane at temperatures less than 1000°C .



Finally, Blocher, Browning and Wilson [8] take the process of silicon production from trichlorosilane one step further by proposing that a closed-cycle regeneration system be used. Their suggested regeneration system consists of two reactors, the decomposer and the regenerator. Silicon is produced in the decomposer. Since the volume of the decomposer is fixed and the rate of SiHCl_3 feed is restricted by the reaction times involved, the advantage of adding hydrogen to the reacting SiHCl_3 is insignificant. The optimum operating condition in this case appears to be one in which the reaction gas composition is 100 percent SiHCl_3 . Therefore, Blocher, Browning and Wilson [8] study the possibility of producing pure silicon by the thermal decomposition of trichlorosilane and in turn of converting the SiCl_4 by-product back into SiHCl_3 .

As shown by Hunt and Sirtl [13] and Yoshizawa, Hashino and Sakaguchi [7] the major silicon containing products in equilibrium with the silicon produced by the thermal decomposition or hydrogen reduction of trichlorosilane at temperatures in the 900°C to 1100°C range are $\text{SiCl}_4(\text{g})$, $\text{SiHCl}_3(\text{g})$ and $\text{SiCl}_2(\text{g})$. Additional species present in significant amounts are $\text{HCl}(\text{g})$ and $\text{H}_2(\text{g})$. The SiCl_2 tends to react with the HCl present to produce SiHCl_3 . Therefore, the major by-products of the reaction are SiCl_4 , H_2 and HCl . Unreacted SiHCl_3 and small quantities of SiH_2Cl_2 and SiHCl_3 are also found in the equilibrium mixture. The SiH_2Cl_2 and SiCl_3 are converted to SiCl_4 and SiHCl_3 through arbitrary reactions with HCl . The SiHCl_3 is then separated out for direct recycling while the SiCl_4 is regenerated into SiHCl_3 .

In the regenerator, SiCl_4 , HCl and H_2 are placed in contact with a bed of granular metallurgical grade (MG) silicon and two important reactions occur.



Blocher, Browning and Wilson [8] attempt to find ways to control these reactions in an effort to maximize the production of SiHCl_3 and minimize the production of SiCl_4 .

To achieve the desired balanced cycle, the HCl is separated out of the SiCl_4 - H_2 - HCl mixture and is added later to quench the reversal of SiCl_2 to SiCl_4 by converting the SiCl_2 into SiHCl_3 . The SiCl_4 and H_2 are fed through a bed of metallurgical grade silicon. The desired regenerative process is one in which the operating temperatures are minimized, the amount of metallurgical grade silicon used is minimized while the yield of SiHCl_3 is maximized. It has been found that by adding the correct amount of hydrogen to the silicon tetrachloride, the process can be controlled such that one mole of metallurgical grade silicon is added to the system in the regenerator for each mole of high purity silicon produced from the SiHCl_3 without excess production of SiHCl_3 or SiCl_4 . It is also found that within the 1127°C to 1327°C range, decreasing the operating temperature of the regenerator requires an increase in the moles of SiCl_4 and H_2 used in order to maintain a constant yield of SiHCl_3 . The regenerative process is not found to be efficient at temperatures less than 1127°C .

Based on these results, it appears that by imposing the correct parameters such as temperature and the H_2 to SiCl_4 ratio, this closed-cycle chlorosilane system has the potential of being an efficient, economical process for producing high purity silicon.

2.4 IMPACT FLAMMIBILITY

A mixture of trichlorosilane and air will explode when initiated by a spark, a heat rod or possibly, ultraviolet light [2]. In addition, Muller, Witte and Beyer [14] found that SiHCl_3 explode on impact if enough SiH_2Cl_2 is added to the SiHCl_3 . An explosion is initially observed in a mixture containing 25 percent SiH_2Cl_2 and 75 percent SiHCl_3 . The SiH_2Cl_2 - SiHCl_3 mixture must contain 25 percent or more SiH_2Cl_2 for an explosion to occur. Some of the older literature on the explosiveness of SiHCl_3 is given in Gmelins Handbuch der anorganischen chemie [2]. Certain results indicate that these earlier samples may have contained some of the more reactive SiH_2Cl_2 .

2.5 STANDARD HEAT OF FORMATION

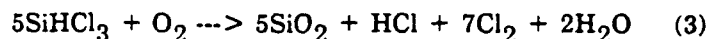
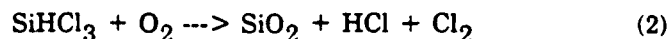
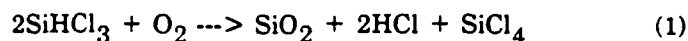
In 1972, Hunt and Sirtl [13] of Dow Corning Corporation calculated the standard heat of formation of gaseous trichlorosilane as part of an effort to determine species concentrations in various equilibrium Si-H-Cl systems. The enthalpy of formation of SiHCl_3 was derived from already existing experimental data. It had been found that the equilibrium molar ratio of SiCl_4 to SiHCl_3 is highly sensitive to the heat of formation of SiHCl_3 used in the calculation when assuming a fixed heat of formation value for SiCl_4 . In addition, it was known that a relatively simple equilibrium exists in the Si-H-Cl system at low temperatures. At temperatures below 1250°K , the gas phase equilibrium mixture contains only SiCl_4 , SiHCl_3 , HCl and H_2 . All the enthalpy values are known with substantial certainty except that of SiHCl_3 . Hunt and Sirtl [13] also studied decomposition reactions of trichlorosilane and silicon tetrachloride, hydrogenation of trichlorosilane and chlorosilane formation resulting from silicon hydrochlorination to arrive at a heat of formation value for trichlorosilane. They conclude that the standard heat of formation of SiHCl_3 is $-116.0 \pm 0.7 \text{ kcal/mol}$.

In 1981, Bell, Perkins and Perkins [15] of Simon Fraser University in Canada calculated the heat of formation of various chlorosilanes in the gaseous phase including SiHCl_3 . Their calculation was based on using the heats of formation of SiH_4 and SiCl_4 given in the 1972 CATCH Tables for Silicon Compounds to find the corresponding heats of atomization and then deriving the bonding parameters for the Si-H bond and the Si-Cl bond. The heat of formation calculated by Bell, Perkins and Perkins for trichlorosilane by this method is -482.4 kJ/mol or -115.3 kcal/mol .

A significant amount of data was used to derive both Hunt and Sirtl's [13], and Bell, Perkins and Perkins' [15] enthalpy of formation values for trichlorosilane. The $-116.9 \pm 0.7 \text{ kcal/mol}$ is based purely on experimental data while the -115.3 kcal/mol value is based on experimental and theoretical correlations. Having no basis upon which to conclude that one method is far superior to the other, the average value of the two, -116.1 kcal/mol , will be used in this work.

2.6 THE COMBUSTION REACTION

Initially, the combustion of trichlorosilane was believed to occur according to one of the following reactions [2, 14].



Muller, Witte and Beyer [14] examined reactions 1 and 2 to determine which appeared to be the combustion reaction. They used potassium iodide to test for the presence of chlorine as a reaction product. A positive reaction indicated that chlorine was definitely one of the combustion products. As a result, reaction 1 was eliminated from further consideration.

The products from reaction 2 [14] are identical to those from reaction 3 [2] with the exception of water vapor which is a product of reaction 3. It is not known at this time whether tests have been done to identify water vapor in the combustion product mixture or if this is a proposed reaction based on theory or similar combustion reactions. Having no basis on which to determine that one of the reactions is the combustion reaction and the other is not, both will be considered in this paper. Once the experimental heat of combustion has been found, it may be possible to estimate which of the two reactions occurs. To completely determine which reaction occurs, samples must be taken directly from the reaction vessel following combustion and analysed, and our apparatus was such that it was not possible to carry this out.

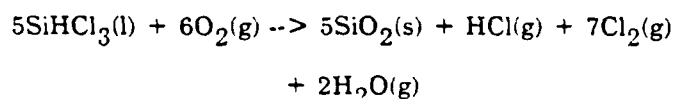
Chapter III

HEAT OF COMBUSTION

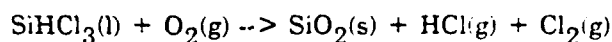
3.1 THEORETICAL HEAT OF COMBUSTION

The theoretical heat of combustion of trichlorosilane is calculated from the heat of formation value of each reactant and product as found in the literature. Again, the following reactions are being considered.

Reaction 1:



Reaction 2:



The literature gives the heat of formation (Δh°_f) of SiHCl_3 in the gaseous phase only. As described in the previous section, two slightly different heats of formation were found for gaseous SiHCl_3 [15, 13]. The value used in this paper of -116.1 kcal/mol is the average of the two.

To proceed with calculating the theoretical heat of combustion for each of the above reactions, the heat of vaporization of SiHCl_3 must be determined. Unfortunately, no information is available that gives the vapor pressure of trichlorosilane as a function of temperature. Resorting to an alternate approach, Trouton's Estimation Method [16] is employed to estimate the heat of vaporization of SiHCl_3 . Trouton discovered that the ratio between the heat of vaporization and the normal boiling point of a liquid is approximately constant, 21cal/mol^o K. This is a good approximation for non-polar molecules.

$$\Delta h_{\text{vap}} / \text{Boiling point} = 21 \text{ cal/mol}^\circ \text{K}.$$

From the Airco Catalogue [17], the boiling point of SiHCl_3 at atmospheric pressure is 89.4°F (31.8°C). The corresponding heat of vaporization for SiHCl_3 is 6.4 kcal/mol . This gives the heat of formation of liquid SiHCl_3 as -122.5 kcal/mol . The standard heats of formation of all reactants and products in the two proposed trichlorosilane combustion reaction are given in the following table.

TABLE 3
Heats of Formation

compound	$\Delta h^\circ_f (\text{kcal/mol})$	Reference
$\text{SiHCl}_3(\text{g})$	-122.5	above
$\text{O}_2(\text{g})$	0	18
$\text{SiO}_2(\text{s, quartz})$	-205.4	18
$\text{HCl}(\text{g})$	-22.063	18
$\text{Cl}_2(\text{g})$	0	18
$\text{H}_2\text{O}(\text{g})$	-57.798	18

Based on the above data, the theoretical heat of combustion for reaction 1 is -110.43 kcal/mol or -815.3 cal/g and for reaction 2 is -104.96 kcal/mol or -774.9 cal/g .

3.2 EXPERIMENTAL HEAT OF COMBUSTION

3.2.1 The apparatus and its operation

A Parr 1421 semimicro calorimeter was used to determine the heat of combustion of SiHCl_3 . Additional accessories required for the operation of the calorimeter were a strip chart recorder, a tank of oxygen, and a chemical balance. The semimicro calorimeter consists of a glass Dewar reaction chamber, a semimicro bomb, a thermistor probe and temperature measurement bridge, all arranged to operate in a single compact cabinet. Connections are provided at the thermometer panel on the top face of the calorimeter

cabinet for connecting the strip chart recorder. The thermistor probe and temperature measurement bridge are designed such that the temperature rise is plotted directly in degrees Celcius on the strip chart recorder for temperature in the ten degree span from 20° C to 30° C.

Samples are burned in the stainless steel semimicro bomb. The bomb is designed to hold and burn samples that range approximately from 0.02 to 2.0 grams and release not more than 1200 calories. The sample is placed in the sample holder , and its net weight is recorded. Then, it is placed in the support loop located off the support post on the underside of the bomb head as shown in Figure 12 below.

Fuse wire, 10 cm. in length, is attached to the two hook terminals on the underside of the bomb cover. Using a small Allen wrench, the wire loop is rotated into a helical coil in order to concentrate the heat on the sample. The electrical connection to this fuse is made by pressing the ignition terminal down onto the terminal nut located on the bomb head. The sample is ignited by passing an electrical current through this coiled fuse wire. Figure 12 has been reproduced from the Parr calorimeter catalogue [20,p.8.] and shows the bomb head with the fuse and sample in place.

Once the sample is placed on the support loop and the fuse wire is attached, the bomb head is placed on the bomb cup and body and is held together by tightening the bomb screw cap with a wrench. When tightly clamped together, the bomb is ready for the oxygen fill procedure. An oxygen fill connection is provided with the semimicro calorimeter allowing the bomb to be filled from a commercial oxygen tank. The gas inlet valve located on the bomb cover is opened and closed by means of a pin wrench inserted through the eye of the valve cap. (refer to Figure 12) The bomb is filled with oxygen by opening the bomb valve, pressing the oxygen fill coupling over the valve cap and slowly opening the needle valve in the fill line until the desired pressure is reached.

At this point, the bomb contains air which if not removed will affect the heat of combustion results. To remove the air from the bomb, the bomb is alternately filled with

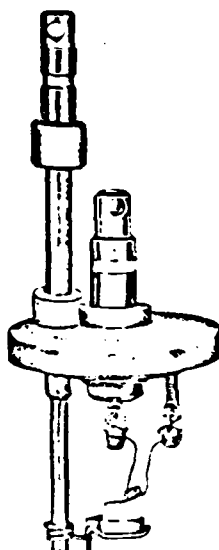


Figure 12: The bomb head with fuse and sample in place.

oxygen to 30 atmospheres and exhausted back to ambient pressure. This purging cycle is repeated four consecutive times prior to the final oxygen fill to 30 atmospheres.

After the final fill, the ignition connection is placed over the terminal nut on the bomb cover and the pressurized bomb is placed in the bomb support loop and hung from the rim of the glass Dewar reaction chamber. The Dewar chamber contains 400 grams of water. The temperature of the water used in this experiment is slightly lower than room temperature. The glass Dewar reaction chamber rests inside a highly polished, stainless steel air can. The air can is designed so that it is unable to absorb or emit any radiant heat, and sits inside a foamed plastic block in the calorimeter cabinet. These three layers serve as an isothermal jacket around the water and bomb such that the jacket temperature remains constant while the water temperature rises. A cover complete with attached

stirrer and a opening for the thermistor probe is placed over the reaction chamber. The stirrer operates by means of a drive belt attached to a small motor and serves to circulate the water to ensure that the heat from the bomb is dissipated quickly and evenly.

The thermistor probe is installed through the cover opening while its opposite end is plugged into the temperature measurement bridge in the calorimeter cabinet. The thermistor probe and bridge are designed to operate within the temperature range from 20° C to 30° C. In this range, the relationship between temperature change and thermistor voltage change is linear. A 100 mV (0.1V) change in output corresponds to a 1.0° C change in temperature. This output signal is fed to the strip chart recorder. The recorder can be set to trace the temperature changes over a full scale of 0.1° C, 1.0° C or 10° C by setting the input voltage on the recorder at 10, 100 or 1000 millivolts respectively.

The calorimeter and strip chart recorder are zeroed before the first run. Before connecting the calorimeter to the strip chart recorder, the recorder is zeroed by short circuiting the input terminals and using the zero control on the recorder to move the pen to zero baseline. Next, the calorimeter is connected to the recorder with the calorimeter switch in the OFF position. The calorimeter remains in this position for a 30 minute minimum period to allow the thermistor to warm up.

The zeroing procedure continues by setting the range switch on the recorder for the desired full range temperature trace, setting the bridge at the desired baseline temperature between 20° C and 30° C, and then, moving the selector switch through each switch position while adjusting the pen to the zero baseline using the corresponding switch position adjustment knobs [19]. The thermistor bridge is zeroed in the ZERO position so that at the balanced condition, the bridge's output voltage is zero. In the NULL position, the bridge is zeroed so that at the set baseline temperature, the bridge's output is zero. In the CAL position, the bridge is zeroed so that the 1000 millivolt output from the calorimeter corresponds to a temperature of 10° C above the set baseline temperature.

The final switch position on the thermometer panel is the READ position. In this position, the location of the pen on the chart indicates the temperature of the water surrounding the bomb corresponding to the baseline temperature setting on the thermistor panel and the full scale trace setting on the recorder.

Before ignition, the recorder speed is set, the pen is dropped and the recorder begins charting the water temperature. The temperature is observed for a few minutes. A slight temperature rise is expected due to small amounts of heat dissipated by the stirrer to the water or conducted from the isothermal jacket to the water. These slight temperature rises prior to ignition must be taken into consideration when determining the overall temperature rise that is used to calculate the heat of combustion. When a linear preignition temperature drift is observed, the sample is ignited by pushing the button on the ignition unit.

The heat of combustion causes the temperature of the combustion products to rise rapidly. This heat is dissipated from the bomb to the surrounding water. The temperature increase is charted until a constant maximum temperature or slight, steady temperature rise (linear postignition temperature drift) is observed.

3.2.2 *The Experiment*

Three good runs were made using the trichlorosilane followed by three runs using benzoic acid tablets for standardizing the equipment. Standardizing the equipment followed the trichlorosilane runs due to the fact that the sample holder used for the trichlorosilane was developed during the actual experiment.

Based on the theoretical heat of combustion values for SiHCl_3 of -815.3 cal/g (reaction 1) and -774.9 cal/g (reaction 2) calculated in Section 3.1 and the criteria that the bomb is not designed to burn samples that release more than 1200 calories, the maximum sample size that could be used was 1.4 grams. The next consideration was to find an appropriate sample holder for the trichlorosilane. Trichlorosilane is extremely volatile and an accurate

value of the mass of trichlorosilane being burned is necessary in order to compute its heat of combustion. The platinum sample dishes provided with the semimicro calorimeter were small and fragile so that covering the dish with tape or plastic wrap to prevent evaporation was impossible. After some searching, this problem was resolved by using a small steel fitting with a nut and bolt to seal one end. This fitting held approximately 0.35 grams of trichlorosilane. Initially, the top of the sample holder was covered with scotch tape to prevent evaporation. Unfortunately, the trichlorosilane proceeded to evaporate through the scotch tape at a rate of approximately 0.05 to 0.08 grams per minute. Next, covering the sample holder with plastic food wrap was tried and proved to be an acceptable method. The plastic wrap provided a good seal and the evaporation rate was monitored at approximately 0.01 grams per minute.

An electronic balance with a sensitivity of 0.01 grams was used to measure the sample and 400 grams of water for each run. When enclosed by a box and covered with plexiglass, the balance fluctuated ± 0.01 grams. To minimize the evaporation of SiHCl_3 , the water was weighed and placed in the Dewar reaction chamber, and the fuse wire was attached to the hooks on the underside of the bomb head prior to filling the sample holder with trichlorosilane. A baseline temperature of 20°C and a full scale trace of 10°C , corresponding to the 0.1 input voltage setting on the recorder, were used in this experiment. The temperature of the water used in each run was approximately 22°C , slightly lower than room temperature.

Transferring the sample amounts of trichlorosilane into the sample holder was always done under the hood. Gloves and safety glasses were also a necessity. A glass pipet with a rubber suction bulb was used to draw a small amount of trichlorosilane out of its bottle and fill the sample holder. When filled, the sample holder was sealed as tightly as possible with a 1.5" by 1.5" piece of plastic wrap and weighed on the electronic balance. After recording the net weight of the trichlorosilane, the sample holder was placed in the sample loop with the fuse wire just touching the center of the plastic and then enclosed in the bomb. This procedure took approximately 30 seconds.

The next step was to remove the air from the bomb by alternately filling the bomb to 30 atmospheres with oxygen and then exhausting the bomb back to ambient pressure. This process was repeated four times. Unavoidably, each time the bomb was depressurized, trichlorosilane vapor was vented along with the air and oxygen. This was immediately detected by the odor of the vented gases. This four cycle air removal procedure took approximately 1.5 minutes. Both of the processes described above were timed so that the amount of trichlorosilane lost by evaporation between the time the sample was weighed and ignited could be estimated.

After the four purging cycles, the bomb was pressurized to 30 atmospheres and put into place. The chart drive was set at a speed of 3 centimeters per minute and the temperature plot was started. When a linear, preignition temperature drift was observed, the sample was ignited.

The same equipment and procedures were used in the standardization runs. The laboratory devised sample holder covered with a 1.5" by 1.5" piece of plastic wrap was used to hold the sample in the bomb. To standardize the calorimeter, a benzoic acid tablet with a heat of combustion of -6318 cal/gram was placed on top of the sample holder and plastic wrap and ignited.

3.2.3 *Results and Discussion*

The experimental heat of combustion of trichlorosilane is calculated from the following equation [19].

$$\Delta H = [-(\Delta T_c)(e) + f + w] / m$$

ΔH represents the gross heat of combustion of the sample at the mean reaction temperature. The rate of temperature rise is rapid in the first few minutes after firing and decreases as the water approaches its temperature maximum. The mean reaction temperature is taken as approximately 63 percent of the total temperature rise and is used to calculate the corrected temperature rise. As mentioned in subsection 3.2.2, a

slight, linear temperature rise caused by the heat dissipated from the stirrer or the environment was observed prior to ignition. A similar slight, linear temperature plot was observed following the temperature rise caused by combustion.

To separate the preperiod and postperiod temperature drifts from the temperature rise caused by combustion, the following method was employed [19]. Straight lines were drawn on the thermogram tangent to the preperiod and postperiod drift lines. The distance, D , between the two tangent lines was measured at a point in the middle of the reaction period. The point at which the distance between the preperiod drift tangent line and the actual temperature plot equals $0.63D$ was found. A horizontal line is drawn through this point intercepting both drift lines. The intercepts correspond to the corrected minimum and maximum temperatures such that the total corrected temperature rise is as follows.

$$\Delta T_c = T_{f,c} - T_{i,c}$$

An example of this graphical analysis is shown for SiHCl_3 Run 1 in Figure 13 at the end of this section.

The fuse correction, f , in the equation above, is given in calories. After each combustion run, the bomb is depressurized and opened and the unburned pieces of fuse wire are measured. The heat contribution of the fuse wire is calculated given that 10 cm. of wire was initially used and the combustion of 10 cm. of fuse wire releases 23 calories. In the same way, w represents the correction for the plastic wrap in calories. Based on previous runs, it is estimated that a 1.5" by 1.5" piece of plastic wrap releases approximately 5 calories when burned, where m is the mass of the sample in grams. And finally, e represents the effective heat capacity of the calorimeter which is determined in the standardization runs by burning a benzoic acid pellet with a known heat of combustion, ΔH , of -6318 cal/g.

Three standardization tests were run using benzoic acid tablets and all of the same equipment used in the trichlorosilane tests. The corrected temperature, ΔT_c , was read

from the resulting thermogram using the process described above. The effective heat capacity of the semimicro calorimeter, e , was calculated from the following equation and the results are tabulated in Table 4.

$$e = [f + w + (m)(\Delta H)] / \Delta T_c$$

TABLE 4

Results of Standardization Runs.

parameters	Run 1	Run 2	Run 3
m, grams	0.18	0.22	0.21
f, cal	15	16	11
w, cal	2	2	2
ΔT_c , °C	7.44	9.18	7.90
e , cal/°C	155.5	153.7	154.0

The effective heat capacity value, e , used to calculate the enthalpy of combustion of SiHCl_3 is 154.4 cal/°C, the average of the three values listed in Table 4.

The heat of combustion of trichlorosilane, ΔH , was initially calculated using the mass measured by the balance. The resulting ΔH value is very low compared with the theoretical ΔH value of -815.3 cal/g for reaction 1 but very close to the ΔH value of -774.9 cal/g for reaction 2. It was observed that the mass of the trichlorosilane sample was reduced by evaporation from the time the bomb was taken off the balance until the bomb was pressurized for the fifth and final time.

The evaporation of trichlorosilane prior to ignition occurred in two steps. First, during the 30 seconds from the time that the bomb was weighed until it was enclosed inside the bomb. During this period, the SiHCl_3 evaporated at a rate of 0.01 grams per minute so that 0.005 grams of SiHCl_3 was lost. Second, during the approximately 1.5 minutes it took to remove all the air from the bomb. The air removal was accomplished by repeating the following cycle four times. The cycle included pressurizing the bomb to 30 atmospheres

with oxygen and then exhausting the bomb back to atmospheric pressure. Each time the bomb was depressurized, SiHCl_3 was detected in the exhaust gases. During the air removal process, the SiHCl_3 evaporated at various rates, the maximum rate being 0.01 grams per minute.

It is difficult to estimate the total amount of trichlorosilane lost during this period due to the fact that the evaporation rate is a function of the bomb pressure. In addition, the trichlorosilane evaporates continuously during the air purging process so that not all of the vapor is removed from the bomb during the air removal cycles. Since it is impossible to measure the amount of trichlorosilane lost from the bomb, the amount must be estimated. It is estimated that 1 minutes worth of evaporation in open air or 0.01 grams of SiHCl_3 is equivalent to the amount of trichlorosilane lost during the air removal process. Therefore, the mass of SiHCl_3 burned is 0.015 grams less than the amount initially measured by the electronic balance. The corrected heat of combustion, ΔH_c , is based on the mass of trichlorosilane that is burned.

Finally, the balance fluctuated continuously ± 0.01 grams during the measurement process. The final corrected heat of combustion includes any variation in the value that balance fluctuations might have caused. The results of the three trichlorosilane runs are tabulated in Table 5 and the temperature plots of the three runs superimposed onto a single graph are shown in Figure 14 at the end of this section. Based on this experiment, the heat of combustion of SiHCl_3 is found to be $-803.8 \text{ cal/g} \pm 3 \text{ percent}$ or in the -779.7 cal/g to -827.9 cal/g range. This is the average value of the three runs. Assuming that the method used in section 3.1 to calculate the theoretical heat of combustion is accurate, the maximum error in this experiment is 4.4 percent based on reaction 1 and 6.8 percent based on reaction 2. The errors are a result of using a balance with a sensitivity of only 0.01 grams and with a fluctuation of ± 0.01 grams as well as the inability to measure the exact amount of trichlorosilane that is lost from the bomb during the air purging process. It is likely that part of the experimental error is due to minor equipment inaccuracies but

these inaccuracies are insignificant in comparison to those caused by the balance and the evaporation of SiHCl_3 .

When estimating the amount of trichlorosilane lost by evaporation between the time the SiHCl_3 was weighed and ignited, every effort was made to ensure accuracy. Nevertheless, if the estimated amount of trichlorosilane lost by evaporation exceeds the actual amount lost, the maximum experimental error based on reaction 1 is too large and the error based on reaction 2 is too small. If the estimated amount is less than the actual amount, the experimental error will be closer to but will not exceed that found for the uncorrected heat of combustion, ΔH . The uncorrected heat of combustion value, calculated from the measured mass of SiHCl_3 , is -761.0 cal/g. This value corresponds to a maximum error of 9.2 percent for reaction 1 and 1.8 percent for reaction 2.

TABLE 5

Results from the SiHCl_3 Calorimeter Runs.

parameters	Run 1	Run 2	Run 3
m, grams	0.29	0.31	0.25
f, cal	15	10	12
W, cal	5	5	5
ΔT_c , °C	1.58	1.63	1.32
T_m , mean reac., °C	21.7	25.8	24.5
ΔH , cal/g	-772.2	-763.5	-747.2
ΔH_c , cal/g	-814.3	-802.3	-794.9

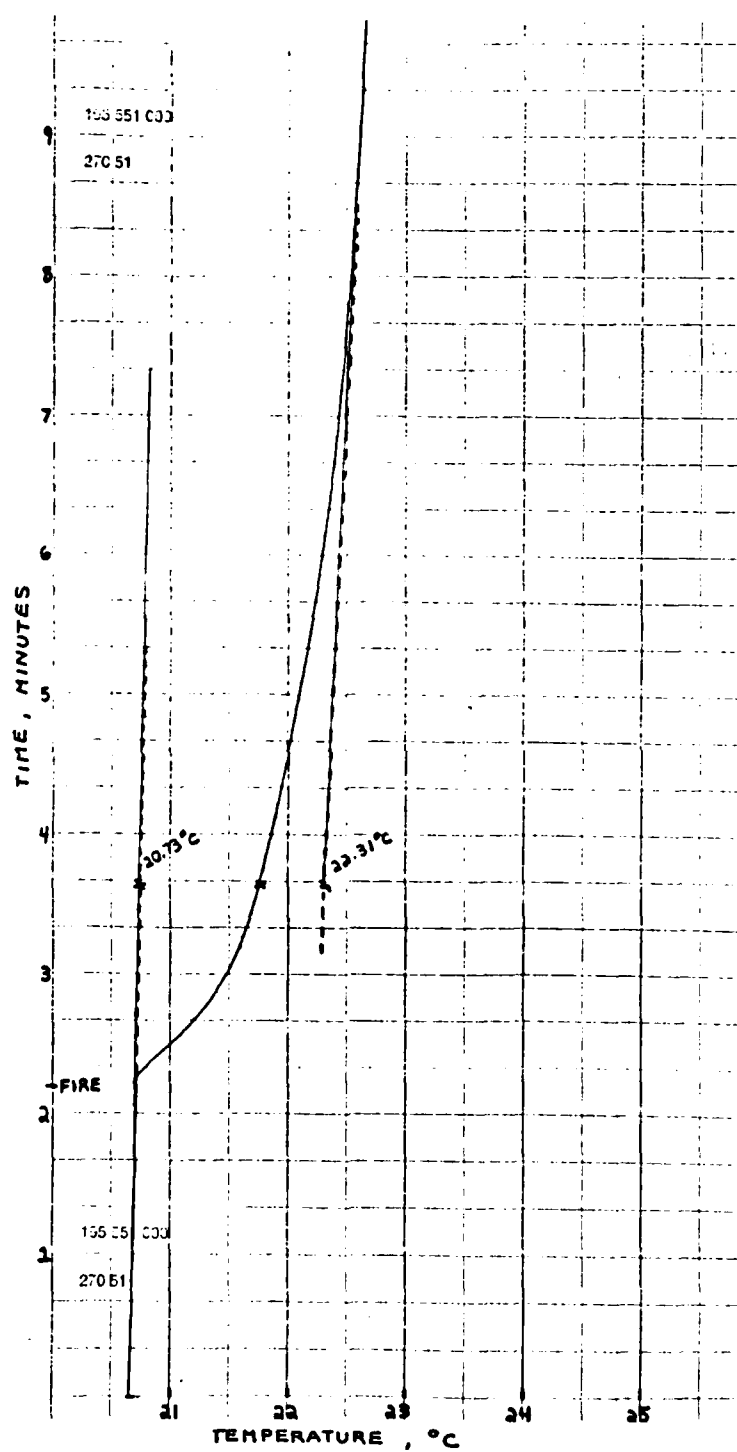


Figure 13: Corrected temperatures for SiHCl₃ Run 1

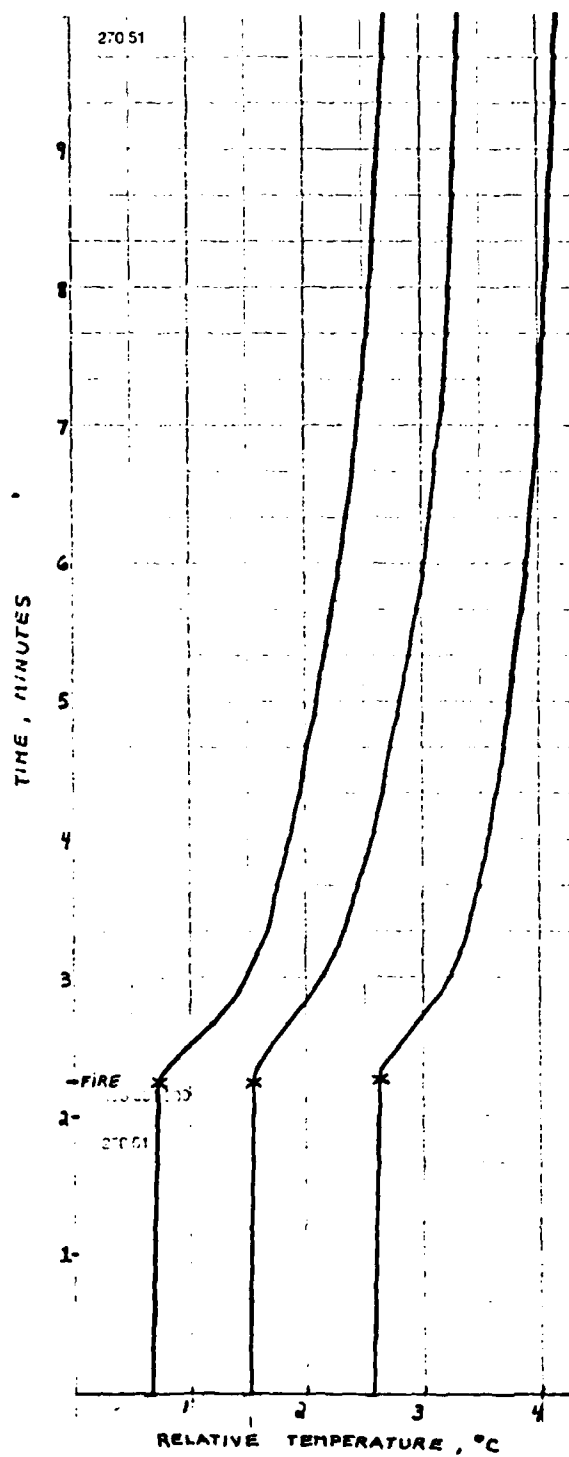


Figure 14: Results of the 3 SiHCl_3 calorimeter runs

Chapter IV

CONCLUSIONS

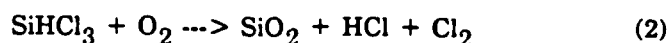
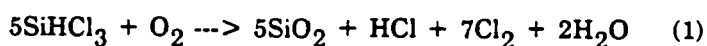
The literature survey section of this paper summarizes many properties and reactions of trichlorosilane. The experimental section describes the combustion experiments performed with SiHCl_3 . In researching and writing this paper, many questions were answered, yet many new ones developed that are left open for further study.

Trichlorosilane does absorb infrared radiation as shown by the IR spectras included in section 2.2. It is not certain whether trichlorosilane absorbs ultraviolet or visible light. It is known that particle formation does not occur when trichlorosilane is irradiated with a 500W xenon lamp or a 500 W high pressure mercury lamp. Particle formation does occur when trichlorosilane is exposed to electron beam irradiation.

Methods used to produce silicon from trichlorosilane are examined in detail. The amount of SiHCl_3 converted to silicon by thermal decomposition is maximum at approximately 1000° C. In addition, the Si deposition rate and the yield of silicon from the thermal decomposition of SiHCl_3 are maximum at 1000° C. Unfortunately, the percent of SiHCl_3 that is converted to Si at 1000° C is only 23 percent. For this reason, hydrogen reduction is often used to increase the yield of silicon from SiHCl_3 .

The ratio of reacted SiHCl_3 to unreacted SiHCl_3 increases as hydrogen is added to the system. If the ratio of H_2 is increased, the dominating reaction changes from thermal decomposition to hydrogen reduction. However, as more H_2 is mixed with the trichlorosilane, the concentration of SiHCl_3 decreases as does the silicon yield and silicon deposition rate. As a result, the optimum method of silicon production is based on economic considerations. In addition, the reaction mechanism, reaction kinetics and a proposed closed cycle regeneration system for the thermal decomposition and hydrogen reduction are discussed in section 2.3.

Little information is available in the literature on the combustion of trichlorosilane. Trichlorosilane is reported to explode in air when initiated by a spark, a heat rod or possibly ultraviolet light [2]. A SiHCl_3 mixture is found to explode on impact when a minimum of 25 percent of the mixture is SiH_2Cl_2 and the rest is SiHCl_3 . The most important question that arose while researching this paper is which of the following two reactions is the combustion reaction of trichlorosilane.



Unable to determine which is the combustion reaction, both are considered in this paper and the theoretical heat of combustion was calculated for both. The theoretical heat of combustion for reaction 1 is -815.3 cal/g and for reaction 2 is -774.9 cal/g.

Unfortunately, the heat of combustion of SiHCl_3 obtained by running combustion tests using a Parr semimicro calorimeter does not indicate which reaction occurs. The experimental heat of combustion was found to be -803.8 cal/g \pm 3 percent. The major sources of error in this experiment are balance fluctuations and the inability to measure the amount of SiHCl_3 that is lost by evaporation between the time the sample was weighed and ignited. Assuming that the theoretical heats of combustion shown above and the method used to estimate the mass of SiHCl_3 lost by evaporation are correct, the maximum error for this experiment is 4.4 percent based on reaction 1 and 6.8 percent based on reaction 2. If the measured mass is used instead of the corrected mass, the heat of combustion is found to be -761.0 cal/g. This value corresponds to a maximum experimental error of 9.2 percent for reaction 1 and 1.8 percent for reaction 2. A more accurate heat of combustion value could be obtained by using a balance with a greater sensitivity as well as having the ability to accurately determine the mass of trichlorosilane that is actually ignited.

Further work must be done in at least two areas before it can be determined whether SiHCl_3 is a feasible reactant for use in particle deposition processes to obtain optical fiber grade silicon dioxide. First, the reaction mechanism of trichlorosilane must be determined. The effect that Cl_2 , HCl , and possibly H_2O product gases have on the SiO_2 product layer should also be considered. Second, additional methods for initiating the combustion reaction should be studied. The absorption spectra of SiHCl_3 in the ultraviolet and visible range should be obtained.

Once this information is available, it should be possible to determine if it is feasible to fill a tube with trichlorosilane and oxygen, initiate the reaction using a laser in possibly the UV range and obtain silicon dioxide. Then, by cooling the tube or using selective product irradiation to promote thermophoresis, the silicon dioxide particles can be forced to the tube wall as desired.

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